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**AFRPL-TR-68-220**

**FLOW DECAY:  
IMPAIRED FLOW IN NITROGEN TETROXIDE  
PROPULSION SYSTEMS CAUSED BY CORROSION  
PRODUCT DEPOSITS**

**Special Technical Report**

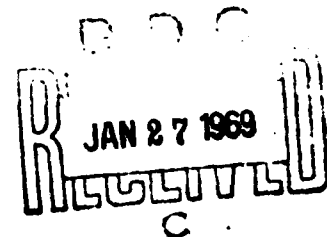
**Chemical and Material Sciences  
Research Division of Rocketdyne  
A Division of North American Rockwell  
Canoga Park, California**

**Technical Report AFRPL-TR-68-220**

**November 1968**

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93523.**

**Air Force Rocket Propulsion Laboratory  
Research and Technology Division  
Edwards, California  
Air Force Systems Command  
United States Air Force**



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Air Force Rocket Propulsion Laboratory  
Research and Technology Division  
Edwards, California  
Air Force Systems Command  
United States Air Force

## **FOREWORD**

This report was prepared in accordance with Contract F04611-68-C-0070, Part 1, Sub-item LAB, and line item B003 of the DD Form 1423. The effort was sponsored by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards Air Force Base, California. The monitoring agency was RPCL; the contract monitor was Mr. B. Biggers.

This special report has been prepared by members of Chemical and Materials Sciences, Rocketdyne Research Division. Dr. E. F. C. Cain (Manager, Engineering and Analytical Chemistry) served as Program Manager and Responsible Scientist. Other contributing personnel were Dr. F. C. Gunderloy, Jr. (Principal Scientist, General and Polymer Chemistry), Dr. J. Sinor (Principal Scientist, Engineering Chemistry), and Dr. R. I. Wagner (Member of the Technical Staff, General and Polymer Chemistry).

This report has been assigned the Rocketdyne Report No. R-7675.

This report contains no classified data abstracted from other reports.

This report has been reviewed and approved.

**W. H. ENEIKE, Colonel, USAF**  
Chief, Propellant Division

#### ABSTRACT

Flow decay is defined as a condition of impaired flow in nitrogen tetroxide propulsion systems caused by the deposition or the accumulation of stainless-steel corrosion products in small valve orifices or in filters. These corrosion productions take the form of either a solid or a second liquid phase, the latter being variously described as very viscous or gelatinous. Both types of deposit are derived from iron nitrate, the solid being assignable the chemical formula  $\text{NOFe}(\text{NO}_3)_4$ , the liquid being a complex mixture derived from the interaction of iron nitrate and water. Both are soluble in the nitrogen tetroxide, but only at a level of a few parts per million (as iron). Their presence in the propellant and their deposition is a function of the water equivalent level of the propellant and the temperature and pressure profiles which the propellant encounters before and during flow. In general, the deposition will occur whenever propellant has been cooled just prior to or during flow and the  $\Delta T$  required for deposition may be as low as 3 to 5 F.

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## INTRODUCTION

During the past few years, several problems associated with impaired flow in nitrogen tetroxide propellant systems have been studied under government and industry funds (Ref. 1, 2, 3, and 4). Concurrent with these studies, reports from test stands operating with NTO propellants, and reports based on the analysis of telemetered data from actual flights, have also indicated that propulsion systems employing nitrogen tetroxide as the oxidizer are subject to unpredictable and sometimes uncontrollable decreases in flowrate.

In the studies cited above, as well as in test stands where the system components have been inspected, it has been shown that it is the accumulation of either solid or liquid (gelatinous) deposits which has resulted in a reduction in propellant flowrate through either valves or filters. This phenomenon, termed flow decay, was usually observed as a significant decrease in flow (10 to 50 percent) and occasionally as a complete stoppage of flow. The conditions required for formation of the deposits and the nature of the deposits both liquid and solid have now begun to integrate into a coherent picture, although much remains to be done to define the system completely.

The relationship between the solid and liquid deposits is only now beginning to emerge. The solid deposit formed in brown NTO has been characterized as a form of iron nitrate,  $\text{NOFe}(\text{NO}_3)_4$ , while the liquid deposit usually formed in green NTO has contained a partially hydrated iron nitrate as a major component. As a working hypothesis, it is suggested that the change in the nature of the iron-containing deposit from solid to liquid is primarily a function of the water equivalent concentration, with elevated temperatures and long storage times contributing significantly. The observations from all sources on formation of iron-containing deposits in NTO, described in this report, appear to fit into the framework of this hypothesis.



## DISCUSSION

### BACKGROUND AND GENERAL SUMMARY

In December 1963, a special flow bench was designed and installed at Rocketdyne's Santa Susana Field Laboratory for the purpose of calibrating drag-body flowmeters in nitrogen tetroxide. The facility was also intended to evaluate other flow measuring devices, such as cavitating venturis, orifices, and turbine meters, under operational conditions with flowing nitrogen tetroxide. The nitrogen tetroxide used was the "brown" material as specified in MIL-P-26539A. After placing the flow bench in operation, an effect which has since been called "flow decay" was noted. This phenomenon was a progressive decrease or decay in the rate of propellant flow through the system with respect to time, with no discernible change occurring in the system conditions.

It was first believed that the problem was one of contamination of the system, but after an extensive program to eliminate all possible sources of contamination, flow decay still occurred from time to time. The first insight into the phenomenon was achieved when a glass-walled throttling valve (sight gage valve) was built and installed in the flow bench. The occurrence of flow decay was found to be simultaneous with the appearance of a yellow crystalline deposit on the needle and shaft of the valve. A study of the effect of operating parameters showed that flow decay could be induced at will by temperature conditioning the oxidizer at a slightly elevated temperature and then reducing the temperature at the same time flow was started. The crystalline deposit was identified as an iron nitrate complex.

At this time, the Rocket Propulsion Laboratory, Edwards Air Force Base, agreed to sponsor a detailed investigation of the problem under Contract AF04(611)-11620 at Rocketdyne (Ref. 2). Under this contract, the solid

deposit was isolated and identified as  $\text{NOFe}(\text{NO}_3)_4$ . The maximum solubility of this material in  $\text{N}_2\text{O}_4$  was found to be on the order of 1 to 4 ppm in terms of iron concentration. Extensive flow bench tests were conducted to determine the effect of various operating parameters and other variables such as valve material and design. It was found that flow decay occurred whenever "brown" nitrogen tetroxide was heated (even to as low as 90 F) in a steel tank, then cooled during flow.

Flow decay was shown to be a reversible solubility phenomenon in that the precipitate formed could be redissolved in the propellant from which it came by reheating the propellant. The experimental behavior observed suggested a process involving a chemical reaction between the nitrogen tetroxide and the stainless-steel tank to form a slightly soluble compound or intermediate in solution. Subsequently, when the temperature was lowered, a saturated or possibly a supersaturated solution was formed which deposited the solid  $\text{NOFe}(\text{NO}_3)_4$  on suitable nucleation sites during flow at the point of temperature or pressure change.

Concurrently, the TRW Systems Group was studying problems associated with valves sticking or jamming, filters plugging, and flow stoppage which had been encountered when flowing "green" nitrogen tetroxide controlled according to the MSC-PPD-2A specification. These problems were attributed to a contaminant residue found on filters and between small clearances of sliding parts within valves. This problem was initially investigated by TRW Systems for NASA under Contract NAS7-107 (Ref. 4), and continued under Contract NAS7-549 (Ref. 5). Under the initial program, it was postulated that complex iron colloids were precipitating out of the  $\text{N}_2\text{O}_4$  propellant, coagulating into a gelatinous mass which clogged filters during  $\text{N}_2\text{O}_4$  flow. The contaminant was described as reddish in color, slimy, and very viscous. The viscous contaminant crystallized to a fine red dust when excess  $\text{N}_2\text{O}_4$  was removed.

Under the latter program, the TRW Systems Group studied the artificial conditioning of  $N_2O_4$  with suspect gel-producing impurities and the corrosivity of  $N_2O_4$  on aluminum, stainless steel, and titanium as a function of selected impurities; i.e.,  $H_2O$ ,  $O_2$ ,  $NOCl$ ,  $Cl_2$ , and  $NOCl + O_2$ . Several flow experiments were conducted. Flow decay and complete blockage was observed with neat "green"  $N_2O_4$  as specified in MSC-PPD-2A when flowed through 0.005- and 0.010-inch-diameter capillaries. A gel material was found to be the cause of flow decay and blockage. It was concluded that iron as well as zinc could react with  $N_2O_4$  to form the gel material.

In the informal verbal discussions between appropriate technical personnel from various organizations and in published reports, it became apparent that two different but somehow related phenomenon were being observed and reported by various workers. Accordingly, an  $N_2O_4$ /IRFNA Conference (Ref. 6) was held in June 1968 at the Aerospace Corporation, El Segundo, California under the sponsorship of the Air Force Rocket Propulsion Laboratory, Edwards, California. Various functions involving research, production, systems operations, transportation, packaging, etc., presented papers covering the problems of  $N_2O_4$  and IRFNA in handling, storage, and use in missile systems. Hypotheses were advanced at this meeting to explain the differences in phenomena which had been observed. Subsequently, under the present contract at Rocketdyne (F04611-68-C-0070), the relationship between the gelatinous and crystalline deposits has been demonstrated and the concentration of water in the oxidizer has been shown to be a critical variable. Differences in the effect of the two kinds of deposits on systems operation have also been demonstrated.

It should be noted that it is not the intent of this report simply to describe the work under Contract F04611-68-C-0070. This report highlights the most important points of this contract, reviews previous work, and shows how all of the current and previous efforts are interrelated. The basis of a unified approach to the problem has thus been established and is discussed in this report.

## ENGINEERING CHARACTERIZATION OF FLOW DECAY

### System Effects

The phenomenon of flow decay in nitrogen tetroxide systems is a function of the in situ formation of solid or gel-like materials which can obstruct the flow through valves, filters, orifices, etc. Flow-obstructing contaminants which may be loaded into the system with the propellant or which may have been present in the system before the introduction of propellant are excluded from consideration. A fundamental knowledge of the factors responsible for this phenomenon has been achieved. The problem can be stated concisely as follows:  $N_2O_4$  in contact with iron reacts to produce slightly soluble iron compounds; under flow conditions, these compounds can precipitate, causing flow decay and eventual flow stoppage. Because all  $N_2O_4$  is exposed to iron during the manufacturing and shipping process, it is expected that any batch of propellant handled in the normal way could be subject to flow decay.

Two distinct types of behavior have been observed (Ref. 2 and 7). When the water content of the propellant is low, a solid, crystalline material identified as  $NOFe(NO_3)_4$  is produced. This material is extremely adhesive and accumulates at all points of flow constriction such as valves, filters, and orifices. When the water content of the propellant is higher, but still within the use limitation of 0.2 percent, pure  $NOFe(NO_3)_4$  is no longer precipitated. Instead, materials of somewhat indeterminate composition involving water are formed which have the appearance of gels or highly viscous liquids. These materials will accumulate and obstruct filters but do not appear to adhere to and cause clogging of valves and macroscopic size orifices. It has now been shown under the present program that solid deposit flow decay can be established in a valve, water can then be added, and liquid deposit flow decay will then begin in a parallel filter. At the same time, flow decay in the valve will disappear.

Dozens of experimental runs in three different flow-bench systems at Rocketdyne have established the characteristics of flow decay as being a constant, gradual buildup of deposit. The rate of buildup is approximately uniform with time, is the same in identical systems flowing in parallel, and is reasonably reproducible on succeeding runs at the same conditions.

#### Necessary Conditions

Flow Decay From Solid Deposits. The solubility limit, in dry propellant, of  $\text{NOFe}(\text{NO}_3)_4$  has been shown to be on the order of 1 to 4 ppm as iron. It has also been determined that a positive temperature coefficient of solubility exists. This provides a basically simple mechanism for the occurrence of flow decay. When  $\text{N}_2\text{O}_4$  has been in contact with iron for a sufficient length of time, a saturated solution of  $\text{NOFe}(\text{NO}_3)_4$  will be produced. Rate-of-solution experiments indicate that equilibrium concentration is reached in no more than a few hours at temperatures of 100 to 120 F. If the solution is then cooled, it will become supersaturated with respect to the flow decay material, and ordinary precipitation will occur. Deposits of the material have been obtained by simply flowing hot  $\text{N}_2\text{O}_4$  past a cold surface. Other methods of producing a supersaturated solution, such as by boiling off a part of the  $\text{N}_2\text{O}_4$ , should also cause precipitation.

Because equilibrium solubility is reached quite rapidly, it is expected that any batch of propellant will contain flow decay material that can be precipitated out by cooling. If the solution is saturated, the amount of cooling necessary for precipitation can be very small. Flow bench runs have been made showing large rates of flow decay with a temperature drop of less than 5 F. The effect of pressure drop during flow is not completely understood as yet. Although temperature drop alone is sufficient to precipitate some material, much more precipitate is obtained as the pressure also is decreased during flow. The magnitude of the pressure drop across the constriction in which flow decay is occurring has an important effect on the rate, but the absolute pressure does not appear to be influential.

Flow Decay From Liquid Droplets. Although the parameters governing the formation of the gel-like materials in propellant of higher water content have not been as well defined, a temperature-limited solubility is again apparently involved. It can therefore be stated that a potential for flow decay exists whenever "moist"  $N_2O_4$  is stored in contact with an iron surface, then subjected to a temperature and/or pressure drop while or before flowing through a filter. The magnitude of flow decay observed, or the amount of deposit formed, is highly variable and dependent on such things as the water content, and the propellant history, particularly in terms of any filtration or heating cycles to which it may have been subjected.

General Considerations. Because the underlying process is based on an equilibrium temperature-solubility curve, the effects of flow decay are reversible (i.e., if the  $N_2O_4$  is heated rather than cooled while flowing, it will dissolve previously precipitated deposits in valves, filters, orifices, etc.). The characteristics of a uniform rate of deposition and temperature reversibility clearly distinguish the phenomenon of flow decay from various propellant contamination and flow plugging problems which occasionally arise on a nonrepeatable basis and have sometimes been referred to as flow decay.

Rocketdyne's experience suggests that when fresh propellant is loaded into a new tank, there may be a period of up to a few weeks required for an initial aging or corrosion of the tank wall before the propellant becomes saturated with flow decay material. A new flow bench system consisting of two 5-gallon stainless-steel tanks and associated plumbing did not exhibit flow decay for almost 3 weeks after propellant was first loaded into the system. However, once the initial period had passed, a re-equilibration of concentration was quite rapid, on the order of 1 hour. The initial time period should be a function of such things as the ratio of tank surface area to propellant volume. Therefore, this time probably will vary from tank to tank, but equilibrium concentration will be reached eventually in all cases. It is also possible that the rate of approach to equilibrium concentration may be a function of temperature, but there are no data bearing on this question.

### Design and Operating Parameters

Solid Deposits. It is seen that the necessary conditions for flow decay may be present in almost any  $N_2O_4$  feed system. However, the existence and precipitation of  $NOFe(NO_3)_4$  (or any of the iron-and-water containing liquids) does not necessarily cause noticeable variations in flow. The concentration of flow decay material in the stream is too small to be detected by analytical or visual techniques. Because the total amount of material involved is no more than a few parts per million, the deposition must be concentrated largely at one point to create a problem. The majority of flow bench experiments has shown a linear decrease in flowrate with time (Ref. 2). Therefore, in a very approximate way, it can be assumed that the rate of buildup of a solid film of  $NOFe(NO_3)_4$  at the minimum flow area is constant for a given set of flow conditions. In a large system, such as a Titan booster, the minute film of solid deposit will probably have no measureable effect. In a small system, however, the results can be catastrophic. Complete stoppage of a 0.25-gpm flow has been observed to occur in less than 1 minute. The decrease in area due to the film, and the resulting decrease in flowrate will be proportional to the ratio of the length of wetted perimeter to the cross-sectional for a constant annular area; i.e., cross-sectional area of propellant flow. This has been confirmed by parallel flow tests with valves of different orifice sizes (Ref. 2).

To obtain a crude estimate of critical system sizes, it may be noted that in a valve with an annular gap of 0.004 inch, it was possible to get complete stoppage of a 0.25-gpm flow in less than 1 minute. Obviously there is a potential hazard for small attitude-control rocket engines in the range of 100-pound thrust or less. As the dimensions of the minimum cross section to flow are increased, the hazard rapidly becomes less. This is because the maximum rate of film buildup remains approximately constant (say 0.002 in./min on all surfaces), and therefore the same

film thickness in a valve with a 0.04-inch minimum opening will obviously have much less effect on flow than in a valve with 0.004-inch opening. This point was illustrated by experiments reported in Ref. 2, p. 94 ff: "Four miniature valves were selected for parallel flow comparisons. Since the flow tests were made with the valves almost completely closed, the minimum cross section to flow was a thin annulus in all cases----. The orifice diameters were 0.065, 0.120, 0.170 and 0.215 inch. ----- For all runs, the valve with the larger diameter orifice exhibited a faster rate of flow decay. The larger the diameter of the valve orifice----- the smaller will be the annular gap between the orifice and the valve stem" (for a given flow rate). Therefore, the valves with the smallest minimum clearance were the most susceptible to flow decay. Also, the ability of the solid deposits to adhere to the surface at the point of minimum cross-section becomes less as the deposit becomes thicker. Because of its lack of mechanical strength, pieces of the solid deposit flake off from time to time and at an increasing rate as the deposit grows thicker. Not enough information is available at present to calculate a set of critical system dimensions independent of the propellant.

A clearly indicated design rule is to make the minimum clearances in a flow system as large as possible. A round orifice should be less susceptible to flow decay than any other shape because it would have the lowest ratio of wetted perimeter to cross-sectional area. Also, sharp-edged orifices should allow thick deposits to flake off more easily than orifices with large L/D ratios. Materials of construction are not of major importance. The deposition of  $\text{NOFe}(\text{NO}_3)_4$  has been observed on steel, aluminum, glass, and plastic. For this reason, avoiding flow decay by control of construction materials does not seem promising once the  $\text{N}_2\text{O}_4$  has been exposed to iron-containing tank materials. However, there appeared to be some differences in the ease with which the solid



deposit adhered to different surfaces. Valve seats and needles made of glass and plastic did not plug up quite as easily as those made of metal, but none of the materials tried was significantly resistant to flow decay deposits.

Another potential hazard from  $\text{NOFe}(\text{NO}_3)_4$  exists in systems which are stopped and restarted. Because it is extremely adherent, a small amount of  $\text{NOFe}(\text{NO}_3)_4$  deposited in a valve (an amount too small to cause any appreciable flow decay) could cause the valve to become jammed in the closed position after shutdown. This has been observed to happen in the flow bench test program.

A factor which can influence flow decay effects in a system is the interaction of components placed in series. The experimental evidence accumulated to date suggests that the bulk of the material contributing to flow decay through a valve or other constriction comes out of solution at the point of pressure drop, and does not exist as a solid upstream of this point. This immediately infers that flow decay cannot be prevented by means of a simple filter. It also points up the fact that if two restrictions are placed in series, the downstream restriction is likely to be affected by material forced out of solution at the first restriction. Therefore, the total flow decay effect in a system cannot be obtained by summing up test results for individual sections tested separately.

Liquid Deposits. The above discussion refers only to the precipitation of solid  $\text{NOFe}(\text{NO}_3)_4$ . To date, the gel-like materials are not known to clog system components other than filters, although either the solid  $\text{NOFe}(\text{NO}_3)_4$  or the gel-like precipitates can cause such plugging. It is in the case of filters that one exception may arise with respect to the general immunity from flow decay enjoyed by large systems. Because the pore size is

the same regardless of the area, a large filter is just as susceptible to flow decay as a small one. Tests with temperature-conditioned  $N_2O_4$  have resulted in serious plugging of the filter in a 2-inch-diameter line. Nonetheless, most large flow system filters have a large enough surface area and small enough pressure drop to be immune to flow decay under normal conditions. Because the actual viscosities are not yet known, it is possible that the gel-like deposits could be forced through a filter with sufficiently large pore size. A test program to investigate various filter parameters is now under way.

Temperature Control as a Potential Solution. A simple method of preventing flow decay of either type and which may be applicable in certain instances is to provide constant temperature control of the entire flow system. However, this control must be quite precise. It was noted previously that a temperature drop of as little as 5 F could produce significant rates of flow decay. Thermal changes in a system could cause complex effects. A slow thermal cycling of the entire system would ensure that the concentration of flow decay material in solution is always equal to its equilibrium value and would not provoke flow decay if no temperature drop occurred during flow. During the decreasing temperature portion of the cycle, a precipitate or second phase might form and collect on the tank walls, or settle to the bottom of the tank. Any material which settled out near the tank outlet could enter the feed system on flow start, but would be removed easily by the system filter. During the warming portion of the cycle, the material would redissolve to maintain equilibrium, and the total amount would not increase from cycle to cycle. Therefore, as long as there were no supersaturation and no temperature drop during flow, the presence of a saturated solution might not produce any observable flow effect.

In contrast to the case of slow cooling and uniform temperature distribution, a more rapid cooling may produce a supersaturated condition in the bulk propellant and cause flow decay, even with uniform temperature throughout the system during the thermal cycle. Also, a decreasing temperature gradient through the system may produce flow decay with or without thermal cycling. The existence of a constant thermal gradient in the propellant would offer another mechanism for possible flow stoppage. Propellant diffusing from areas of high temperature to low temperature and back could tend to build up deposits at the low-temperature points. If this material were accumulated at an unfavorable spot, a large amount might be carried suddenly into the feed system on flow startup. This type of mechanism has been proposed as an explanation for an incidence of flow plugging on a large test stand after a long period of inactivity (Ref. 6).

Use of Additives as a Potential Solution. The approach studied by Rocketdyne for the elimination of flow decay from nitrogen tetroxide systems is the use of chemical additives to form soluble complexes with the iron-containing flow decay compounds. In the initial effort (Ref. 2) several suitable organic compounds were identified and tested in an experimental flow bench system. Acetonitrile, benzonitrile, pentafluorobenzonitrile and ethyl acetate were all shown to be effective (at a concentration of 0.25 percent) in dissolving deposits of  $\text{NOFe}(\text{NO}_3)_4$  from the flow system. During the initial stages of the current program (Ref. 7), these additives were also found to be effective in removing solid deposits in PPD-2A propellant ( $\text{N}_2\text{O}_4$  + 0.6 percent NO). However, it has been determined that the efficiency of all these additives gradually deteriorates under high-temperature storage conditions. There are marked differences in the period of effectiveness. The best of these additives, acetonitrile, was stable and effective for at least 2 weeks at 130 F, but deteriorated in approximately 2 weeks at 150 F. None of the additives have been effective in removing the gel-like second phases which are formed in high-water-content propellant. Several inorganic coordinating agents are currently under consideration and show some promise of being both stable and effective.

Water may be considered as an additive which is effective, at a concentration of 0.2 percent in preventing the formation of solid  $\text{NOFe}(\text{NO}_3)_4$ . The gel-like materials which result may, in limited cases, be considered less of a hazard because they apparently are primarily a filter problem and do not actually block valves and orifices. However, the mechanical factors of valve sticking or jamming might still remain a problem, as work by the TEW Systems group has shown (Ref. 4). The exact concentration of water which causes a transition from a system which precipitates solid  $\text{NOFe}(\text{NO}_3)_4$  to one which produces the gel-like materials has not yet been determined.

#### LABORATORY CHARACTERIZATION OF FLOW DECAY

##### Solid Deposits

Identification of Solid Deposit. The solid deposit first observed in March 1965 in a sight gage valve (Ref. 1) was isolated in an inert atmosphere from the valve stem for determination of its physical and chemical properties. No melting of the solid was observed under a pressure of  $10^{-3}$  torr at temperatures up to 120 C (248 F) at which temperature the solid sublimed. The chemical composition of the deposit varied but was clearly indicated to be a solvated ferric nitrate,  $\text{Fe}(\text{NO}_3)_3 \cdot x\text{N}_2\text{O}_4$ . The value of  $x$  ranged between 7 and 1.2 with higher values obtained, when the handling time required to isolate and hydrolyze the sample was at a minimum. This apparent loss of  $\text{N}_2\text{O}_4$  on standing in the absence of a nitrogen tetroxide atmosphere was subsequently confirmed when larger amounts of laboratory-synthesized material became available.

The infrared spectrum of the solid deposit (Fig. 1) was determined (Ref. 1 and 2) and correlated well with the synthetic material (Ref. 1). The absorption bands indicate a  $\text{NOFe}(\text{NO}_3)_4$  structure for  $\text{Fe}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_4$  (Ref. 3).

X-ray diffraction powder patterns of synthetic material have shown two crystal forms, one of which matches the actual flow decay deposit (Ref. 2). Limited studies of the synthetic material and related compounds using nmr ( $H^1$  and  $N^{15}$ ), nqr, epr, and Mossbauer spectroscopy (Ref. 2) were not particularly informative.

It should be noted that solid  $NOFe(NO_3)_4$  is extremely hygroscopic, and it will absorb water rapidly from the atmosphere, liquifying and undergoing hydrolytic reactions to evolve  $N_2O_4$ . It loses considerable bulk during this process, so that a large crystal, upon exposure to the open air for a short period, will be reduced to little more than a moist brown stain. Accordingly, unless components are carefully handled in dry inert atmospheres during disassembly procedures, the final material isolated may not actually represent the state of the original deposit. In fact, the final "stain," if exposure to moisture has occurred, may even be small enough or spread thin enough to be overlooked. This behavior was one of the impediments in the earlier attempts to isolate and identify the material.

Once the hydrolytic reactions have run their course, it is sometimes possible to dry the material and form a solid again. Some  $NOFe(NO_3)_4$  may be present in this redried deposit, but the major components are more likely to be iron nitrate hydrates, iron oxide, and/or iron oxynitrates. Partial or complete solidification of liquid deposits has been observed by both Rocketdyne and the TRW Systems group.

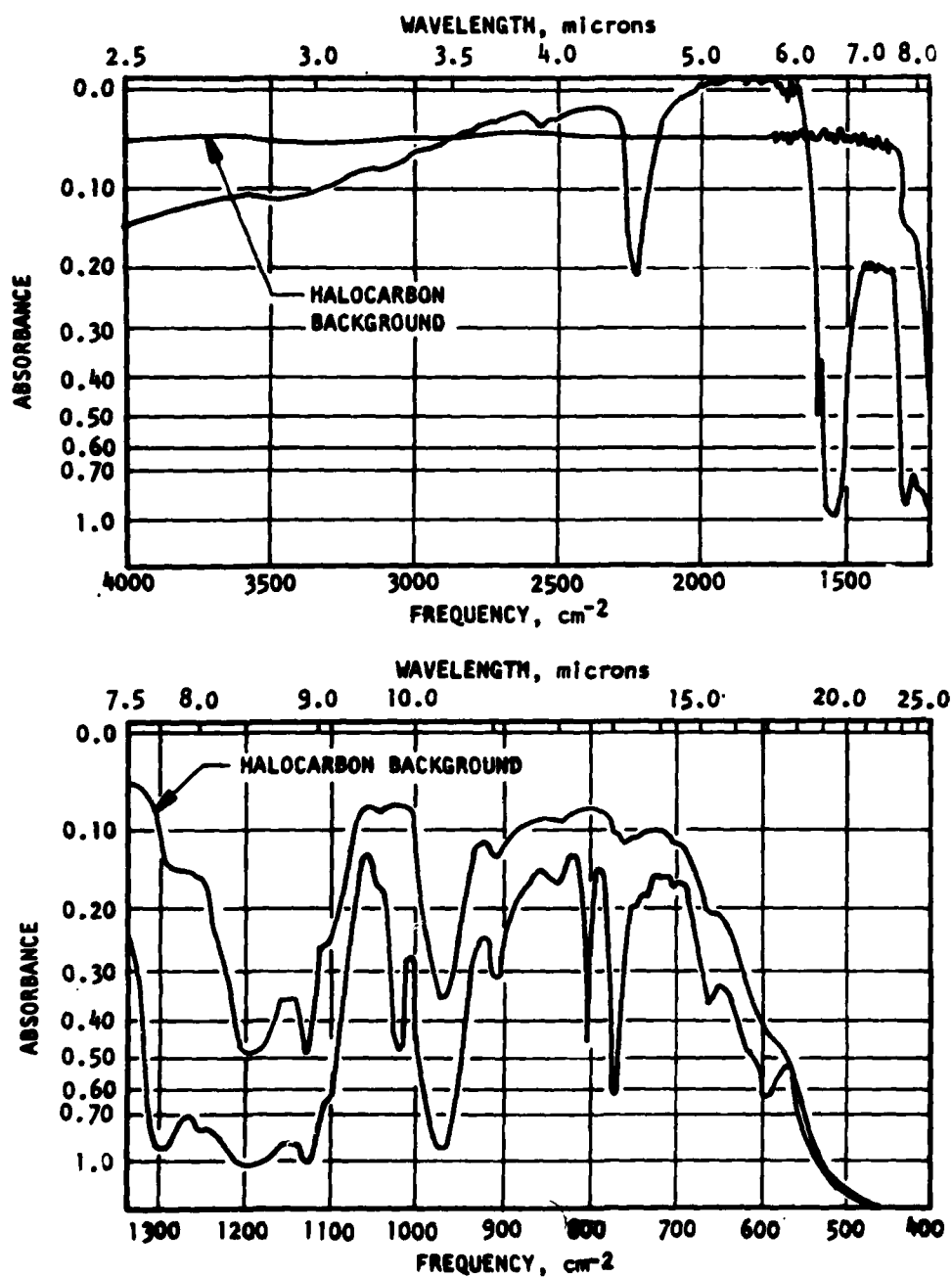


Figure 1. Infrared Spectrum of Crystalline Flow-Decay Compound ( $N_2O_4$  Flow Test Facility)

Solubility of Synthetic Flow Decay Compound,  $\text{NOFe}(\text{NO}_3)_4$ . Solubility data have been obtained usually by hydrolysis of saturated NT0 solutions followed by analysis for iron content. The results are therefore no better than the accuracy and precision of the iron analysis. Preliminary values were obtained in propellant grade NT0 using a modified colorimetric method (nitroso-R-salt) and are in the range 6 to 8 ppm of iron (Ref. 1). Subsequent determinations (Ref. 2) were made in oxygenated distilled anhydrous iron-free  $\text{N}_2\text{O}_4$  by both colorimetric (o-phenanthroline) and atomic absorption spectrophotometric (AAS) methods at a series of temperatures between 0 and 37.8 C (32 and 100 F). Average values were 0.4 ppm (0 C), 0.8 ppm (25 C), 0.9 ppm (30 C), and 1.0 ppm (37.8 C) although data were scattered in the range 0.1 to 2.6 ppm. The effects of added NO (up to 1 w/o) and water (up to 0.5 w/o) were also separately studied at 25 C and only the latter had a significant effect on the solubility, increasing it to approximately 4 ppm at the maximum water concentration.

Deposition of Solid Flow Decay Compound in Laboratory Apparatus. A small flow decay apparatus, basically consisting of two 1-liter stainless-steel tanks connected through a small glass ice-cooled U-trap, was successfully used to produce from propellant grade brown NT0 a solid deposit identical by IR spectrum to that formed in engineering hardware (Ref. 2). With green NT0 (0.2 w/o  $\text{H}_2\text{O}$  equivalent) saturated with synthetic  $\text{NOFe}(\text{NO}_3)_4$  in a similar apparatus, a solid deposit was produced in the glass U-trap which showed the same behavior as the above natural flow decay compound (Ref. 7). Optimum heating time to obtain a recognizable solid deposit was 2 to 3 days at 55 to 60 C (130 to 140 F) for brown NT0 in stainless steel and 1 to 2 hours at 65 to 68 C (150 to 155 F) for the green NT0- $\text{NOFe}(\text{NO}_3)_4$  mixture at maximum use specification water concentration (0.2 w/o). However, under more extreme conditions of temperature, or with prolonged heating time, liquid deposits were obtained from the same propellant.

Dissolution of Solid Flow Decay Compound in Laboratory Apparatus. Screening tests for solvents or co-solvents with NT0 for  $\text{NOFe}(\text{NO}_3)_4$  have been conducted (Ref. 2). Compounds which were capable of solubilizing  $\text{NOFe}(\text{NO}_3)_4$  and appeared compatible with NT0 were tested as dilute (0.25 w/o) solutions both for their effectiveness in dissolving predeposited flow decay compound and for preventing further deposition of solid material. Five candidate additives, acetonitrile, trifluoroacetonitrile, benzonitrile, perfluorobenzonitrile, and ethyl acetate, were selected as most promising for further evaluation, particularly their effective life. Of these, only acetonitrile has been tested to destruction, which required between 7 and 14 days at 65 to 68 C (150 to 155 F) for 0.25 w/o solution in green NT0 (Ref. 7).

#### Liquid Deposits

Occurrence and Identification of Liquid Deposit. As noted above, green NT0 at the 0.2 w/o water equivalent level, saturated with synthetic  $\text{NOFe}(\text{NO}_3)_4$  gave solid deposits after an initial heating cycle of 1 to 2 hours at 65 to 68 C (150 to 155 F). However, the same tank of material, after a subsequent heating cycle to only a slightly higher temperature (68 to 71 C, 155 to 160 F) for a somewhat longer time, deposited small droplets of viscous liquid that adhered tenaciously to the walls of the cooled glass U-trap. Repeated passages of the propellant resulted in gradual buildup and coalescence of the material into larger drops and "blobs," which were ultimately carried to a side-arm of the trap and removed for analysis. This phenomena has since been duplicated with several batches of propellant at the 0.2 w/o water equivalent level, and it has become evident that solid  $\text{NOFe}(\text{NO}_3)_4$  in the propellant can be converted to the liquid by either an elevated or prolonged preliminary heating cycle.

It should be noted that there was excess (undissolved)  $\text{NOFe}(\text{NO}_3)_4$  present in the propellant tank during these tests. In the flow bench, there is available only a relatively smaller amount of  $\text{NOFe}(\text{NO}_3)_4$  produced by actual



corrosion of the tanks. Under flow bench conditions, the liquid material seems to form without excessive heating or prolonged times. It thus appears that the relative levels of iron nitrate and water, as well as temperature and time, are important in forming liquid deposits.

No positive identification of the dark viscous liquid (or gelatinous) flow decay deposit has been made. Analyses of the liquid deposit gave ratios of  $\text{Fe}/\text{NO}_3^-/\text{NO}_2^- = 1/3.72/1.92$ . Although these data are not sufficient for characterization of the iron species present, they imply the presence of a partially hydrated iron nitrate or iron oxynitrate possibly dissolved in either  $\text{N}_2\text{O}_4$  or  $\text{N}_2\text{O}_4\text{-HNO}_3$  mixture.

Additional evidence of a synthetic rather than analytical nature implies that the viscous deposits are iron nitrate-related compounds. When green NTO, doped with the viscous NTO-immiscible liquid formed in the reported synthesis of  $\text{NOFe}(\text{NO}_3)_4$  (Ref. 8), was flowed through filters or capillaries a viscous liquid deposited partially or completely blocking the flow (Ref. 5). Also relevant is the synthesis from  $\text{FeCl}_3$  and anhydrous  $\text{HNO}_3$  of solid  $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$  which is first isolated as a viscous liquid (Ref. 9).

The conversion of solid  $\text{NOFe}(\text{NO}_3)_4$  to a liquid upon exposure to atmospheric moisture was noted earlier.

Solubility of Liquid Deposit. No quantitative solubility data are available because the nature of the liquid itself is not clearly defined. Visual comparison of the quantity of liquid and solid deposits obtained per kilogram of green iron-saturated NTO under given conditions suggests the solubility is near that of the solid  $\text{NOFe}(\text{NO}_3)_4$  deposit (Ref. 6).

Deposition of Liquid Flow Decay Compound in Laboratory Apparatus. Clogging and plugging of both glass capillaries and stainless-steel filters by gelatinous materials was first reported by the TRW Systems Group (Ref. 5). TRW used green NTO (MCS-PPD-2A) having the composition: NTO, 99.0 w/o; NO, 0.85 w/o;  $\text{H}_2\text{O}$  eq. 0.06 w/o. In tests with 0.005-inch and 0.010-inch-diameter capillaries, formation of a dark colored gel was observed with  $\Delta T$ 's from the

hold tank to capillary inlet of 0 to 12 C. NTO flow was markedly reduced or stopped completely, unless  $\Delta P$  across the capillary was in excess of 62 psig for the smaller and 25 psig for the larger capillary.

The fact that TRW obtained a liquid deposit with a system of very low water equivalent in this work is the one unresolved conflict between the work done at Rocketdyne and that done at TRW. Barring sampling and analytical errors, or the inadvertent pickup of water during testing, the TRW data would thus indicate that liquid deposits can form, if conditions are appropriate, even at water levels where Rocketdyne has detected only solid thus far. Some of the current work at Rocketdyne, where studies aimed at defining the conditions for conversion of  $\text{NOFe}(\text{NO}_3)_4$  to liquid deposits are underway, may well resolve this final point of conflict.

With 2 to 10 $\mu$  stainless-steel screen filters flow was almost completely stopped when  $\Delta T = 16$  to 18 C was maintained from the hold tank to filter inlet in the TRW studies. Under the same conditions, the same behavior was observed when the NTO had been doped with a 1:1 mixture of crude synthetic NTO adducts of zinc and ferric nitrates. The amount of ethyl acetate (the synthesis medium, which would oxidize to give an appreciable water equivalent) possibly introduced with the doping agents appears not to have been determined.

As described earlier, Rocketdyne has now observed a dark viscous liquid deposit (Ref. 7) in an ice-cooled 2.5-millimeter-diameter glass U-tube using green NTO (MCS-PPD-2A) with a 0.2 w/o  $\text{H}_2\text{O}$  equivalent in a stainless-steel system. Across the glass test section,  $\Delta T$  of ca. 90 F and  $\Delta P$  of ca. 90 to 100 psig were maintained. Saturation of the propellant with iron compounds was accomplished by introduction of 3.8 grams  $\text{NOFe}(\text{NO}_3)_4$  per 770-milliliters NTO in the run tank. In some runs, solid was either co-deposited with the liquid or partial solidification was observed after several days in contact with the propellant.

A deposit of the same appearance was observed under the same conditions using the same green NTO (0.2 w/o  $H_2O$  eq. plus 0.25 w/o acetonitrile) but only after 2 weeks of heating at 150 to 155 F which oxidized the acetonitrile, thus increasing the water equivalent.

The appearance of a second liquid phase in NTO-containing iron compounds also has been reported in static systems by several laboratories. A dark viscous liquid phase was observed (Ref. 2) when brown NTO (0.9 w/o  $H_2O$  eq.) was heated at 30 C with iron powder for periods in excess of 188 hours; with  $NOFe(NO_3)_4$  as the iron source, a viscous liquid phase formed in NTO (0.47 w/o  $H_2O$  eq.) on standing at ambient temperature. A viscous oil was observed to form (Ref. 5) during 4-months contact of green NTO (0.91 w/o  $H_2O$  eq.) with 347 stainless-steel corrosion coupons.

Addison, et al (Ref. 8) indicate a viscous liquid intermediate product in the synthesis of  $NOFe(NO_3)_4$  from  $FeCl_3$  in an NTO-ethyl acetate mixture. Similarly, evaporation of a mixture of  $FeCl_3$  and anhydrous  $HNO_3$  yield a viscous gum which requires several days to crystallize as  $Fe(NO_3)_3 \cdot 2H_2O$  (Ref. 9).

Dissolution of Liquid Flow Decay Compound in Laboratory Apparatus. Dilute solutions (0.25 w/o) of acetonitrile, trifluoroacetonitrile, benzonitrile, and ethyl acetate in green NTO (0.2 w/o  $H_2O$  equivalent) are ineffective in dissolving the dark viscous liquid and the co-deposited solid flow decay compounds formed by flowing green NTO (Ref. 7). Preliminary work under the present program at Rocketdyne indicates that fluorides (e.g., HF,  $PF_3$ ) interact chemically with the liquid, but this information has not yet been translated into a demonstration of flow decay prevention with such an additive.

## CONCLUSIONS AND RECOMMENDATIONS

The phenomenon of nitrogen tetroxide flow decay can appear whenever propellant, either military specification  $N_2O_4$  or  $N_2O_4$  + varying quantities of  $NO \leq 1$  percent, which has been in contact with iron is cooled just prior to or during flow. Two different types of behavior are observed, depending primarily on the water content of the propellant. At low water concentrations, a solid precipitate,  $NOFe(NO_3)_4$ , is formed which adheres to flow constrictions in valves, orifices, filters, etc. At higher water concentrations, this solid material disappears and a gel-like or viscous liquid phase appears which can clog filters. The total amount of material involved is governed by solubility limitations and is on the order of parts per million of the bulk propellant. Actual flow blockage in rocket engine system components other than filters is thus considered to be an operating hazard only in small systems having minimum dimensions on the order of a few thousandths of an inch.

The malfunction of valves or other components with moving parts could occur due to the adherence of solid  $NOFe(NO_3)_4$  in quantities too small to cause any appreciable decay in flowrate. Filter clogging would occur in any system having insufficient filter area.

Flow decay can be prevented by careful temperature control of a system. However, such control may be impractical because only very small temperature drops can induce significant rates of flow decay. Thermal cycling and the presence of thermal gradients in a system can cause complex effects with respect to the formation of flow decay material.

Although some design guidelines for minimizing the effects of solid deposits (minimize the ratio of wetted perimeter to cross-sectional area at flow restrictions, use sharp-edged orifices, separate components in series, etc.) have been developed, complete elimination of this form of flow decay through system design does not appear feasible.

The use of chemical additives has been only partially successful to date. Water, considered as an additive at 0.2 w/o can be used to restrict the type of deposit to one of liquid or gelatinous characteristics rather than the adherent solid  $\text{NOFe}(\text{NO}_3)_4$ . Whether or not such a restriction would allow for the design of a flow decay-free system has yet to be demonstrated.

Before a final solution to the problem of flow decay can be formulated, there is a considerable amount of additional information that must be amassed. The major points to be covered are described below.

A careful definition must be made, both in the laboratory and on the flow bench, of the conditions under which solid deposits or liquid deposits exist (or co-exist). This definition should be made in terms of iron level, water equivalent level, temperature, age of the propellant mixture, and flow conditions. Physical characterization of the liquid, such as density, viscosity, and surface tension should be carried out.

Flow bench experiments with emphasis on the behavior of the liquid as related to filtration parameters (pore size, material of construction, design, etc.) must be carried out.

A laboratory device amenable to the testing of fluoride-containing additives should be developed, and the chemical reactivity of fluorides with the liquid deposits evaluated in terms of actual flow-decay prevention. With results from such studies in hand, it should be possible to achieve:

1. Criteria for assessing the susceptibility of a given NT0 propellant composition to flow decay under projected use conditions
2. A "fix" for liquid deposit flow decay based on either the filter design or an additive

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<p>Flow decay is defined as a condition of impaired flow in nitrogen tetroxide propulsion systems caused by the deposition or the accumulation of stainless-steel corrosion products in small valve orifices or in filters. These corrosion productions take the form of either a solid or a second liquid phase, the latter being variously described as very viscous or gelatinous. Both types of deposit are derived from iron nitrate, the solid being assignable the chemical formula <math>\text{NOFe}(\text{NO}_3)_4</math>, the liquid being a complex mixture derived from the interaction of iron nitrate and water. Both are soluble in the nitrogen tetroxide, but only at a level of a few parts per million (as iron). Their presence in the propellant and their deposition is a function of the water equivalent level of the propellant and the temperature and pressure profiles which the propellant encounters before and during flow. In general, the deposition will occur whenever propellant has been cooled just prior to or during flow and the <math>\Delta T</math> required for deposition may be as low as 3 to 5 F.</p>		

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